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Evaluation of X-Ray Fluorescence Analysis for the Determination of Arsenic, Vanadium, Cadmium, Lead, and Mercury in Various Matrices

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P. A. Pella, R. L. Myklebust, M. M. Darr, and K. F. J. Heinrich

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16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

Limits of detection for arsenic, vanadium, cadmium, lead and mercury have been determined with a wavelength-dispersive or energy-dispersive spectrometry, or with both, in various matrices consisting of cupric oxide, ferric oxide, lead oxide, coal and fly ash.

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EVALUATION OF X-RAY FLUORESCENCE ANALYSIS FOR THE DETERMINATION OF ARSENIC, VANADIUM, CADMIUM, LEAD AND MERCURY IN VARIOUS MATRICES

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Evaluation of X-ray Fluorescence Analysis for the Determination of Arsenic, Vanadium, Cadmium, Lead and Mercury in Various Matrices

ABSTRACT

Limits of detection for arsenic, vanadium, cadmium, lead and mercury have been determined with a wavelength-dispersive or energy-dispersive x-ray spectrometer, or with both, in various matrices consisting of cupric oxide, ferric oxide, lead oxide, coal and fly ash.

1. INTRODUCTION

The limits of detection have been determined for arsenic in cupric oxide and in ferric oxide, for vanadium in cupric oxide, ferric oxide, lead oxide, coal, and in fly ash, for cadmium in cupric oxide, for lead in cupric oxide and in ferric oxide, and for mercury in coal. Limits of detection for mercury in coal have already been determined and reported in NBSIR 75-675 and are included as an addendum to this report. Measurements were made with either a wavelength-dispersive x-ray spectrometer or an energy-dispersive instrument, or, in some cases, with both. Samples were prepared by adding known amounts of NBS Standard Reference Materials to the matrix of interest and grinding to obtain a homogeneous sample. To obtain concentrations of an element in the 10 to 100 ppm range, successive dilutions of the sample with the matrix material followed by grinding were required.

2. EXPERIMENTAL

The energy-dispersive instrumental arrangement used in this work differed to some extent from that described previously [1]. A commercially available system was used consisting of a tungsten target x-ray tube for exciting various secondary emitters. These consisted of titanium,

Table 1. Instrumental Conditions

	Wavelength Dispersive[b]			Energy Dispersive				
Sample[a]	X-ray Conditions	Bragg Crystal	Counting Time in Seconds	W Tube Conditions	Sec. Emitter	Live[d] Time in Seconds	In Air	In Vac.
As in CuO	Mo-45kV, 45mA	LiF	500	30kV, 10mA	Mo[c]	500	yes	--
As in Fe_2O_3	--	--	--	30kV, 25mA	Mo	500	yes	--
V in CuO	Mo-47kV, 47mA	Graphite	500	25kV, 10mA	Ni	500	--	yes
V in Fe_2O_3	Pt-48kV, 48mA	LiF	500	--	--	--	yes	--
V in Coal	--	--	--	20kV, 3.5mA	Ni	900	--	yes
V in Fly Ash	--	--	--	20kV, 3.5mA	Ni	900	--	yes
Cd in CuO	Cr 40kV, 25mA	Graphite	500	--	--	--	yes	--
Pb in CuO	Mo 45kV, 45mA	LiF	500	31kV, 11mA	Mo	500	yes	--
Pb in Fe_2O_3	--	--	--	30kV, 17mA	Mo	900	yes	--

[a] X-ray lines measured were as follows: AsKα, VKα, CdLα, and PbLα.

[b] Collimation: 102 mm (in length) X 0.51 mm (spacing) + 15.8 mm X 0.25 mm.

[c] Mo secondary emitter including a Mo thin foil filter.

[d] Live time is actual counting time corrected for dead time. That is: Live time $\simeq$1.5 X clock time.

nickel, molybdenum and tin, which were very effective because these monochromatic x-ray lines could be selected to provide the most efficient excitation conditions for analysis of the elements in the sample. A 16-position sample holder was also constructed at NBS in order to obtain good reproducibility on replicate measurements. The instrumental conditions used for each type of spectrometer are summarized in table 1.

Samples were prepared by addition of known amounts of NBS-SRM's or pure reagents to the various matrices of interest followed by grinding in a mortar and pestle. In table 2 is a summary of the reagents employed. Successive dilution of the samples with the matrix was performed to obtain concentrations of an element in the 10-100 ppm range. One-gram samples of the powders were then added to Somar* cups and subsequently analyzed.

Table 2. Known Samples

NBS-SRM No.	Compound Name
83c	Arsenic trioxide
1052b	13.0% V in Bis(1-phenyl-1, 3-butanediono) oxovanadium (IV)
1053a	24.8% Cd in cadmium cyclohexanebutyrate
1059b	36.7% Pb in lead cyclohexanebutyrate

The organo-metallic compounds were selected because of their relatively low concentrations of the element of interest. These required fewer dilutions to be made in order to obtain concentrations in the low ppm range. The copper oxide matrix was prepared from oxidation of copper metal

*Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

(NBS-SRM 45d). The ferric oxide and lead oxide were analytical reagent grade, and the coal and fly ash were NBS-SRM's 1632 and 1633, respectively.

3. MEASUREMENTS AND RESULTS

The limit of detection is often used to characterize the sensitivity of a particular analytical technique for certain trace analysis problems. Because of the numerous and sometimes inconsistent definitions of a detection limit that appear in the literature (see reference 2 for example), it is important to specify how it is defined. For the purpose of this report, the method proposed by Currie [2] is used. An equation can be written for a detection limit based on Poisson counting statistics such as

$$C_{t\ell} = C_{STD} \frac{4.65\sqrt{N_o}}{N_{STD}-N_o} \qquad (1)$$

where $C_{t\ell}$ is the lowest limit of detection theoretically obtainable of the element of interest for a single measurement in concentration units (ppm); C_{STD} is the known concentration (ppm) of that element in the standard; N_o is the total number of counts corresponding to the background or blank in some known time interval; and N_{STD} is the total number of counts (i.e., gross counts) from the standard in the same time interval. Substitution of x-ray intensities for the background and net signal intensities of the standards in the above equation yields a concentration level which should lead to a detected result with 95% confidence. This equation is identical to the one which appears in a previous report [1] except for the numerical constant 4.65. This constant is used when as few as two measurements are made of the background and sample (e.g., paired observations). The quantity $(N_{STD}-N_o)/C_{STD}$ is usually referred to as the sensitivity in ppm^{-1} and is tabulated along with x-ray intensity data in table 3.

Table 3. Data Summary

Samples	Conc. ppm	Net peak counts (av)	Background counts (av)	n[e]	s (counts)[f]	$t^{g}_{.95}$	$N_o^{1/2}$	Sensitivity ppm^{-1}
Wavelength-Dispersive								
As(CuO)	10,000	--	--	--	--	--	--	
	250	19,533						
	100	9,398						97
	50	5,299	33,522	10	200	1.833	183	
	10	1,930						
$As(Fe_2O_3)$	200	--	--	--	--	--	--	--
	50							
V(CuO)	50	21,893	173,752	3	1200	2.920	417	438
$V(Fe_2O_3)$	100	13,538	18,740	5	61	2.132	137	143
	50	7,558						
V (coal)	17.5	--	--	--	--	--	--	--
	7.0							
V (fly ash)	70							
	35	--	--	--	--	--	--	--
	14							
V(PbO)	200	--	--	--	--	--	--	--
Cd(CuO)	250	3,229	22,191	7	127	1.943	149	13
Pb(CuO)	125	5,319	35,409	3	136	2.920	188	42.5
$Pb(Fe_2O_3)$	200	--	--	--	--	--	--	--
	100							
	50							
Energy-Dispersive								
As(CuO)	10,000	23,718						
	250	643						
	100	260	94	3	12.9	2.920	9.7	2.6
	50	140						
	10	41						
$As(Fe_2O_3)$	200	629						
	50	242	236	3	13.7	2.920	15.4	4.0
V(CuO)	50	4,901	5,500	4	56	2.353	74	98.0
$V(Fe_2O_3)$	100							
	50	--	--	--	--	--	--	--
V (coal)	17.5	10,217	4,223	4	84	2.353	65	536
	7.0	2,766						
V (fly ash)	70	38,030						
	35	28,849	11,193	4	280	2.353	106	543
	14	14,554						
V(PbO)	200	2,515	1,472	3	56	2.920	38	12.6
Cd(CuO)	250	--	--	--	--	--	--	--
Pb(CuO)	125	245	105	3	13	2.920	10.2	1.8
$Pb(Fe_2O_3)$	200	861						
	100	364	311	9	18	1.860	16.8	4.0
	50	83						

[e] n is the number of replicate measurements of the background.

[f] estimated standard deviation of a single measurement of the background.

[g] Student's t based on (n-1) degrees of freedom.

A limit of detection based on measurement data can also be calculated according to reference [2], if the variability of the blank is known or can be measured. If n replicate measurements of the blank are made and the standard deviation (i.e., s) of a single measurement is computed, then an experimental limit of detection (C_{exp}) can be calculated according to the equation

$$C_{exp} = C_{STD} \frac{2\sqrt{2}\ t\ s}{N_{STD}-N_o} \qquad (2)^*$$

where t is Student's t [3] based on n-1 degress of freedom. Limits of detection for arsenic, vanadium, cadmium, and lead were calculated according to the above equations and are tabulated for comparison in table 4.

It is interesting to compare the variability of the background tabulated in table 3 for each type of spectrometer. Of course, if the variability is computed according to equation 1, where it is equal to $N_o^{1/2}$, then the only contribution to the random error is assumed to be due to the Poisson statistics of error. The limit of detection calculated in this manner represents the lowest limit theoretically obtainable. If the standard deviation is computed such as in equation 2, then the total contribution to the random error is included in the calculation of the detection limit and will necessarily include experimental sources of random error (e.g., the effect of ambient temperature variations). It should be emphasized, however, that systematic error is not included in these calculations and should be considered separately.

Comparison of the computed standard deviation (i.e., column 6, table 3) with the $N_o^{1/2}$ values via the chi-square test indicated that the Poisson error is the primary contribution to the random error in most cases. The chi-square

*The factor $2\sqrt{2}$ is due to comparison of the unknown with the blank, and that $L_D \approx 2L_C$.

Table 4. Limits of Detection for As, V, Cd, and Pb in Various Matrices Calculated from Equations 1 and 2

Matrix	As		V		Cd		Pb	
	C_{tl} in ppm	C_{exp} in ppm	C_{tl} in ppm	C_{exp} in ppm	C_{tl} in ppm	C_{exp} in ppm	C_{tl} in ppm	C_{exp} in ppm
CuO	(1) 8.8	10.6	(1) 4.4	23.0*	(1) 53	53	(1) 20.5	26.0
	(2) 17.3	40.6	(2) 3.5	3.8	(2) --	--	(2) 26.4	59.0
Fe_2O_3	(1) --	--	(1) 4.5	2.5			(1) --	--
	(2) 17.9	28.0	(2) --	--			(2) 19.5	23.0
Coal	--		(1) --	--				
			(2) 0.56	1.0				
Fly Ash	--		(1) --	--				
			(2) 0.91	3.4*				
PbO	--		(1) --	--				
			(2) 14.0	36.3				

(1) wavelength-dispersive
(2) energy-dispersive
* - variability of background exceeds Poisson contribution

values were exceeded for V in CuO and for V in fly ash, and indicate that the background variability can be attributed to other sources.

Limits of detection for arsenic and lead in coal, and in fly ash could not be accurately determined because of the AsKα-PbLα x-ray line interferences. Efforts to obtain samples of coal and fly ash containing lower concentrations of As and Pb were not successful. Poor results were obtained for cadmium because the background in all cases was very high and the signal level was generally too low with both types of x-ray spectrometers. Vanadium in ferric oxide, however, could not be measured accurately with the energy-dispersive spectrometer because of the interference of the vanadium Kα line with the escape peak caused by the FeKα x-ray line.

4. CONCLUSION

The statistical limits of detection for arsenic, vanadium, cadmium and lead were determined in various matrices consisting of copper oxide, iron oxide, lead oxide, coal and fly ash. In general, the lowest limits of detection were obtained for vanadium in the various matrices with an energy-dispersive spectrometer. These results can be explained on the basis of the generally low background in the x-ray energy region of vanadium and the high excitation efficiency of the nickel secondary emitter. In contrast, a high detection limit for cadmium (i.e., 70 ppm) in copper oxide was obtained.

5. REFERENCES

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[2]. Currie, L. A., Anal. Chem. 40, 586 (1968).

[3]. Natrella, M. G., Experimental Statistics, NBS Handbook 91, table T-5 (1963).

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ADDENDUM

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EVALUATION OF X-RAY FLUORESCENCE ANALYSIS FOR THE DETERMINATION OF MERCURY IN COAL

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Evaluation of X-ray Fluorescence Analysis for the Determination of Mercury in Coal

ABSTRACT

Limits of detection for mercury in coal have been determined on both a wavelength-dispersive and an energy-dispersive x-ray spectrometer. They are between 2 and 3 ppm under best conditions for both spectrometers. Techniques for reducing the background intensity measured by the energy-dispersive system are discussed along with methods of preparing coal specimens for analysis in both instruments.

1. INTRODUCTION

The mercury content of natural coal ranges between 0.05 and 0.4 parts per million (ppm) according to both atomic absorption analysis and neutron activation analysis [1]. Even though the mercury concentration is so low, the large amount of coal burned each year liberates tons of mercury into the environment. Many different analytical procedures are needed to monitor both the sources and the emissions of toxic materials such as mercury. The primary objective of this work is to experimentally ascertain the sensitivity, by x-ray fluorescence analysis, for the detection of mercury in coal.

We have selected two instrumental arrangements for testing the limit of detection of mercury in coal by x-ray fluorescence. The data thus produced should serve as a guide to the configuration of apparatus most appropriate and sensitive for trace determinations by x-ray spectrometry.

The first (energy-dispersive) arrangement consisted mainly of an x-ray tube and a Si(Li) detector with a multichannel pulse height analyzer. Primary x-rays emitted by the tube excite the specimen which emits an x-ray spectrum characteristic of the elements in the specimen. The secondary x-rays are analyzed by the Si(Li) detector which produces electrical pulses proportional in height to the energy of the

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respective x-ray photons. After amplification, these pulses are sorted and stored by the multichannel analyzer. Since this system simultaneously collects all of the x-ray lines emitted by the specimen, the concentration of every element for which there is an x-ray line may be determined at the same time. Therefore, this system is useful for the analysis of the major constituents in a multi-element specimen. The scattering by the specimen of continuous radiation generated in the x-ray tube produces a background which makes it difficult to detect elements present in trace quantities. To reduce this scattering and thus the background, either secondary x-ray targets or x-ray filters can be introduced between the x-ray tube and the specimen.

The second (wavelength-dispersive) arrangement is a commercial single-channel x-ray spectrometer with crystal dispersion. Primary x-rays emitted by an x-ray tube are also used to excite the specimen. The crystal spectrometer is aligned so that the characteristic x-ray line to be measured is diffracted by the analyzing crystal into the scintillation detector. The pulses from the detector are amplified and counted. Since this detector is not flooded with x-rays other than the line of interest, and has a considerable loss in intensity due to diffraction by the analyzing crystal, a higher power may be used on the x-ray tube than with the energy-dispersive system. The peak signal measured with this system is generally higher than that measured with the energy-dispersive system.

Since the peak signal and background signal are measured consecutively with the wavelength-dispersive system, any instrumental drift limits the useful length of time for measurements. Drift is not a limitation with the energy-dispersive system since both the peak signal and background signal may be simultaneously measured. We found that the limit of detection for mercury in coal is about 2 ppm with either

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system. However, to obtain similar results, the energy-dispersive system must operate for about ten times as long as the wavelength-dispersive system. These results are in agreement with the conclusions reached by Gilfrich et al. [2] who made similar comparisons of equipment for the analysis of air pollution samples, and with the conclusions of Leyden [3] on environmental water analysis.

The techniques employed in this work are now being applied to determine the limits of detection of other elements (Pb, As, Cd and V) in coal and in several other materials, such as fly ash, Fe_2O_3, PbO and CuO. We are also trying to further improve both of our systems.

2. EXPERIMENTAL

2.1 Energy-Dispersive System

The primary x-rays emitted by the x-ray tube contain both characteristic x-ray lines from the target (Mo, Pt, etc.) and continuous radiation. The most efficient excitation of an x-ray line in a specimen is obtained when the energy of a strong primary x-ray line from the tube is slightly higher than the excitation potential of the x-ray line in the specimen. The continuum generated by the tube also excites x-ray lines in the specimen; however, part of it is scattered by the specimen, particularly from one of low atomic number, such as coal. This scattered radiation produces a high x-ray background (figure 2a). Since, at a given signal intensity, the limits of detection of any element are lowest when the line-to-background ratio is highest, it is desirable to decrease the background. Three methods of separating the continuum component from primary x-rays can be employed:

1. Use the x-ray tube to excite a secondary target which in turn excites the specimen (figure 2b).

2. Use a filter between the x-ray tube and the specimen to preferentially absorb the continuum (figure 2c).

3. Use a crystal monochromator to diffract a primary x-ray line from the tube onto the specimen.

The first two methods have been applied to measure the limit of detection for mercury in coal. With the energy-dispersive system, we have produced efficient excitation of both the HgLα and $HgL\beta_1$ x-ray lines while reducing background radiation. The first apparatus constructed used a silver anode x-ray tube to excite a pure secondary molybdenum target (see fig. 1). X-rays from this target are in an efficient energy interval (12-15 keV) and do not cause line interferences. A Si(Li) solid-state detector and multichannel pulse-height analyzer (MCA) are used for detection.

We have replaced the original device by a more permanent and versatile configuration. Since molybdenum tubes are more common for x-ray fluorescence than silver tubes, a molybdenum anode x-ray tube has been substituted for the silver anode tube, and a pressed pellet of Y_2O_3 has replaced the molybdenum secondary target (fig. 2b). The HgLα x-ray line is effectively excited by the yttrium K-lines from the Y_2O_3 target which have an energy of about 15 keV and are strongly excited by the molybdenum tube.

In another modification to the system, the Y_2O_3 pellet was placed directly in front of the window of the x-ray tube (fig. 2c). In this arrangement, most of the x-ray radiation generated by the tube is absorbed in the 1 mm thick Y_2O_3 pellet. The YKα x-rays generated in the pellet are of sufficient intensity to efficiently excite the HgLα x-ray line in the specimen.

2.2 Wavelength-Dispersive System

The wavelength-dispersive system used was a standard commercial x-ray fluorescence unit. For the measurement of the $HgL\alpha_1$ x-ray line, a LiF crystal and a scintillation detector were used. Since a molybdenum anode x-ray tube

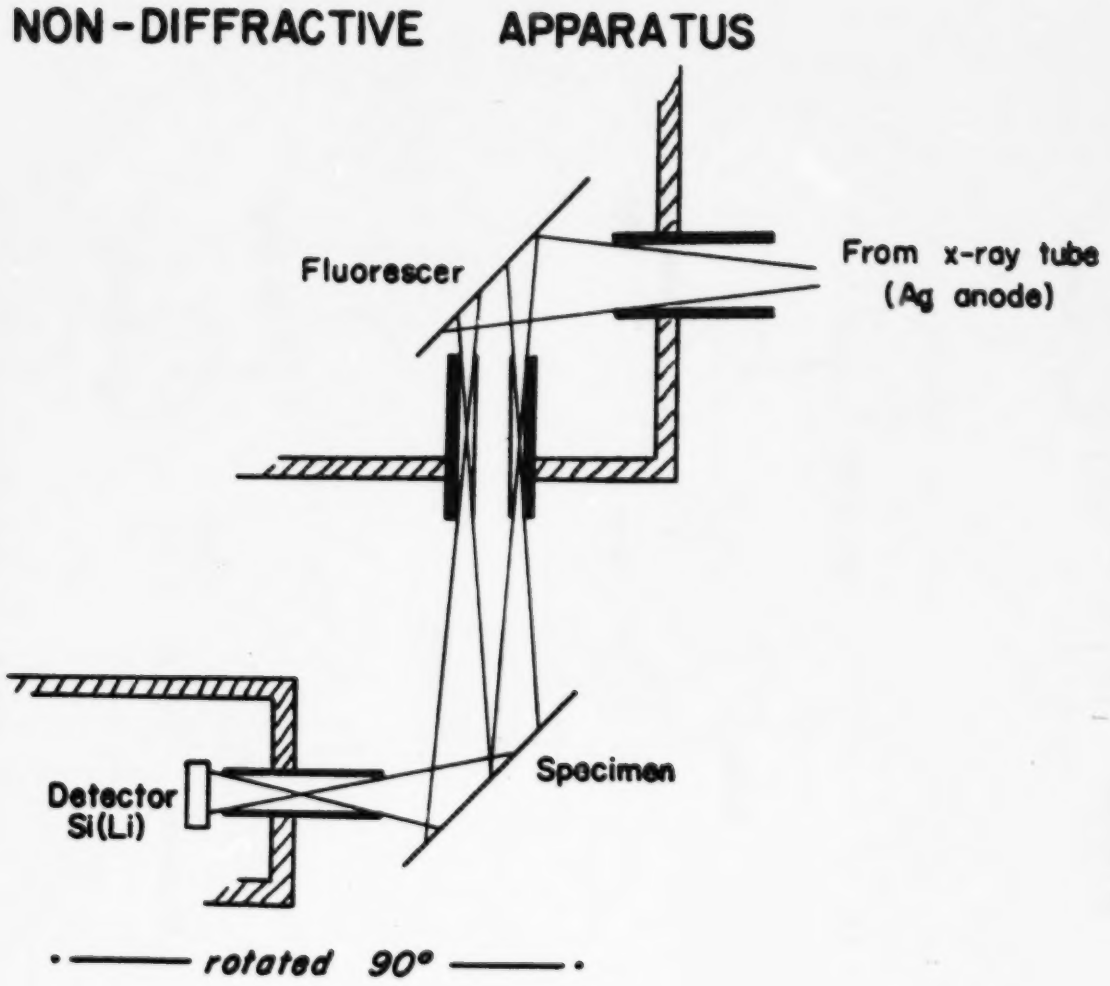

Figure 1. NBS energy-dispersive (non-diffractive) x-ray fluorescence apparatus.

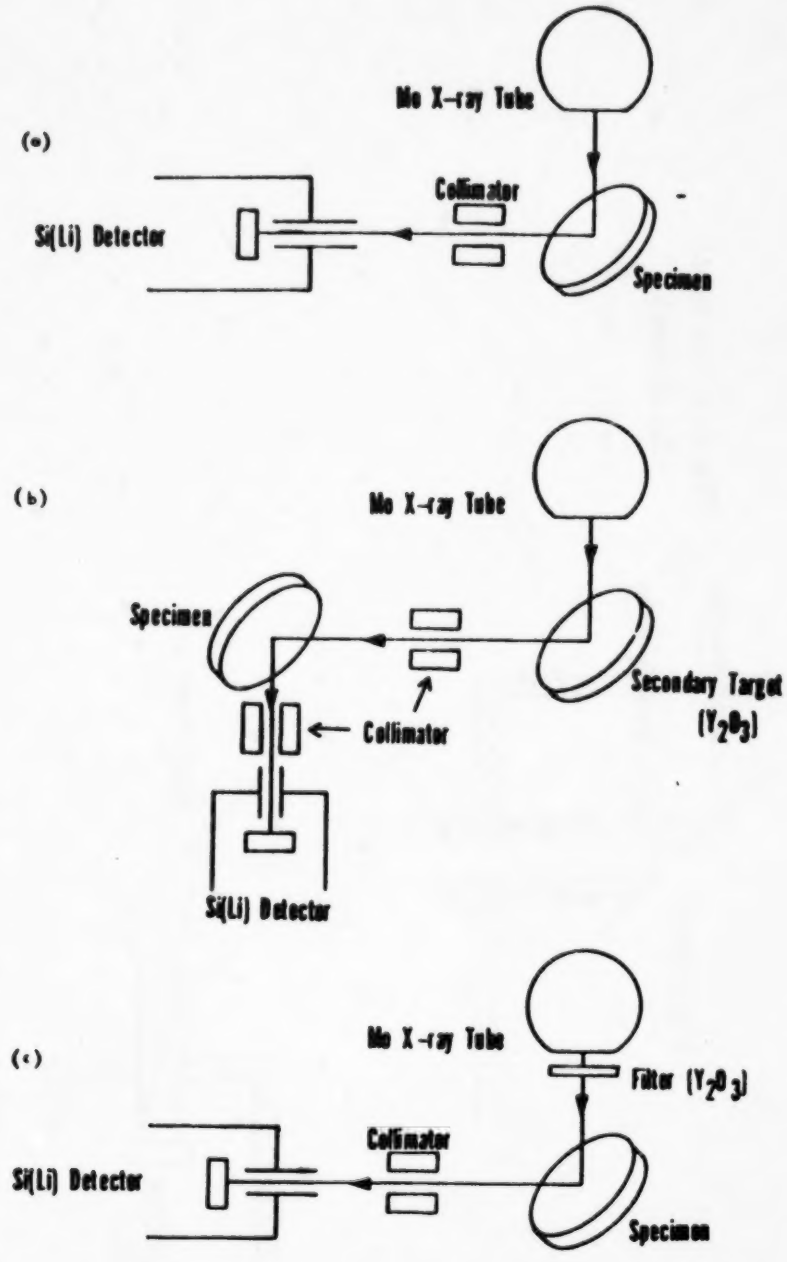

Figure 2. Instrumental arrangements of the energy-dispersive x-ray fluorescence equipment. (a) direct excitation of specimen by x-ray tube; (b) excitation of specimen by secondary target; (c) excitation of specimen by x-rays filtered to remove continuum.

produces energies in the range efficient for the excitation of the mercury lines without generating any interfering x-ray lines, this tube was selected for the work.

In addition to the molybdenum tube, platinum, tungsten and chromium tubes were available. The chromium anode tube could not be used since it does not emit an x-ray line of sufficient energy to excite HgLα. Both the platinum anode and tungsten anode tubes had to be ruled out because of interferences with the analytical x-ray lines of mercury. A brief comparison of the tried configurations is shown in table 1.

Table 1
Comparison of Equipment

	EDS[a]-1	EDS-2	EDS-3	WDS[b]
X-ray tube	Ag	Mo	Mo	Mo
Secondary fluorescer	Mo	Y_2O_3	Y_2O_3	--
Filter	--	--	Y_2O_3	--
Fluorescent x-ray line	MoK_α	YK_α	YK_α	MoK_α
Crystal	--	--	--	LiF
Detector	Si(Li)	Si(Li)	Si(Li)	Scintillation
Read-out	MCA	MCA	MCA	Scaler
Line measured	HgLα	HgLα	HgLα	HgLα

[a]EDS is Energy-Dispersive System

[b]WDS is Wavelength-Dispersive System

2.3 Specimen Preparation

One NBS Standard Reference Material (SRM 1630)** was available for the determination of mercury in coal. This SRM contained 0.13 ppm of mercury, and was used as a base material to which known amounts of mercury were added. For example, a 100 mg specimen was prepared by placing 100 mg of SRM 1630 powder (-325 mesh) on a sheet of 6 μm Mylar* and adding 0.1 ml of trichloroethylene which, upon drying, causes the powder to form a cake. After it had dried, 0.001 to 0.025 ml of a solution of mercuric cyclohexanebutyrate (NBS SRM 1064) in toluene was added to the cake.

Several different methods of mounting specimens for x-ray fluorescence analysis were tried.

1. The specimen was confined to a diameter of 13 mm and held between two sheets of Mylar.

2. The specimen was confined to a diameter of 25 mm and held between a sheet of Mylar and a filter paper backing.

3. The specimen was confined to a diameter of 25 mm and held between two sheets of Mylar.

4. The specimen was pressed into a pellet 12.5 mm in diameter and held between Mylar sheets.

Homogeneity tests were made on three 500 mg specimens mounted by method 3 and on two 500 mg specimens mounted by method 4 (all doped at the 50 ppm Hg level). In the case of method 3, the specimens were prepared and the mercury measured. They were then stirred while in their same mounts and remeasured. No significant difference in the mercury

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measurements was observed. Measurements on both sides of two different pellets mounted by method 4 also showed no significant differences.

Coal specimens containing 10, 20 and 50 ppm of mercury were mounted by the four techniques above. Specimens of 20 mg, 100 mg and 500 mg were mounted by methods 1, 2 and 3. For method 4, 100 mg, 300 mg and 500 mg specimens were pressed. The 100 mg specimens were very thin and difficult to handle.

3. MEASUREMENTS AND RESULTS

The theoretical limit of detection will be defined as that concentration which yields a signal three times as high as the background [4]. Individual pulses arrive at a statistically varying rate, and the number of pulses accumulated in fixed time intervals, for a given specimen and stable instrumental conditions, varies according to a Poisson distribution. Therefore, the theoretical standard deviation of the measured background is equal to the square root of the number of pulses collected from the background.

If N_o is the total number of counts collected at the background, the theoretical limit of detection (C_{tl}) for one measurement can be calculated with the following equation:

$$C_{tl} = C_{std} \frac{3\sqrt{N_o}}{N_{std} - N_o}$$

where C_{std} is the concentration of the measured element in the standard, and N_{std} is the number of counts collected from the standard in the same time interval from that element in the standard. This equation is based on the fact that at low concentrations, the calibration curves are linear in x-ray fluorescence analysis.

If multiple measurements are made on the blank and on the specimen, the experimental limit of detection may be

calculated from the standard deviation (σ) of the mean of the blank determinations. If we have n measurements of the background (X_i), σ may be calculated with the following equation:

$$\sigma = \frac{n \sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2}{n(n-1)}.$$

If the mean of the background counts is estimated as:

$$\bar{X} = \frac{1}{n} \left(\sum_{i=1}^{n} X_i\right)$$

we can calculate an interval from $\bar{X} - t\sigma/\sqrt{n}$ to $\bar{X} + t\sigma/\sqrt{n}$ which we expect, with a certain confidence, to bracket the true background. The factor t is a function of the number of measurements and of the confidence level desired [5]. Therefore, for an element to be detected, the line signal must exceed the mean of the background measurement by more than $t\ \sigma/\sqrt{n}$. The true limit of detection may then be calculated with the following equation:

$$C_{cl} = C_{std} \frac{t \frac{\sigma/\sqrt{n}}{N_{std} - N_o}}{N_{std} - N_o}.$$

Several experiments were performed on the wavelength-dispersive apparatus to determine the experimental limit of detection for mercury in coal. A 200 mg specimen containing 0.125 weight percent of mercury was mounted by method 2 discussed earlier and a wavelength scan was made to check for any possible interferences (see fig. 3). As can be seen in this figure, the background for HgLα is much lower than the background for HgLβ_1. For this reason, the HgLα x-ray line was chosen for all analyses.

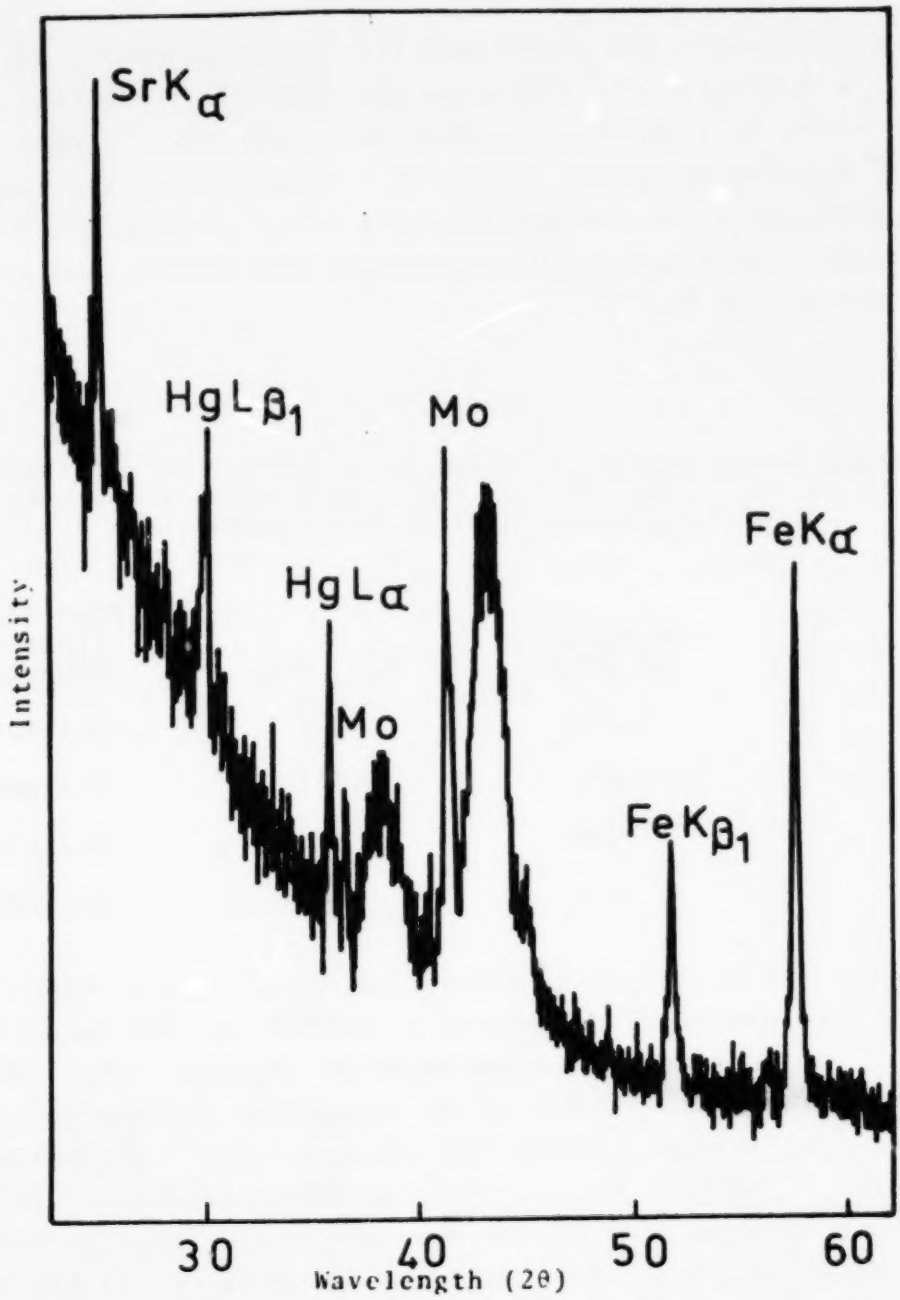

Figure 3. Wavelength scan of coal containing 0.125% Hg.

Optimum operating conditions for the molybdenum x-ray tube were determined by measuring the peak signal-to-background ratio on a 500 mg coal specimen containing 10 ppm mercury mounted by method 2, and on a similar coal specimen without mercury. On the basis of the results listed in table 2, all subsequent wavelength-dispersive measurements were made at 45 keV and 40 mA.

Table 2

100-Second Measurements of 10 ppm HgLα in Coal with Different Operating Conditions for the Molybdenum Anode X-ray Tube Wavelength-Diffraction (LiF) Technique

keV	mA	Background on Blank	HgLα Peak	Theoretical Limit of Detection
50	40	16584	1524	2.5 ppm
45	40	13410	1508	2.3 ppm
45	30	10289	950	3.2 ppm
35	35	8090	585	4.6 ppm

Three 500 mg specimens containing 10, 20 and 50 ppm mercury were prepared and mounted by method 2. The results of 100-s measurements are summarized in table 3. The lowest achievable theoretical limit of detection for mercury is 2.3 ppm. The 50 ppm specimen and the blank were each measured five times. The experimental limit of detection for a 99% confidence interval was 7.5 ppm mercury for the mean of five measurements; however, when the blank was measured 15 times, this limit of detection decreased to 1.6 ppm.

The various specimen-mounting procedures are compared in table 4. Each point is the result of a single 100 s count. Since methods 1 and 3 give the best results, they appear to be the best techniques for sample preparation.

Table 3
Theoretical Limits of Detection in One 100-s Measurement
Wavelength-Dispersive Technique
on 500 mg Specimens with Paper Backing

	50 ppm	20 ppm	10 ppm
Signal (counts)	3092	2112	1574
Background (counts)	13414	13429	13379
Standard Deviation (σ)[t]	115.8	115.9	115.7
S/N (Signal/σ)	26.7	18.2	13.6
Theoretical Limit of Detection	5.6 ppm	3.3 ppm	2.2 ppm

Table 4
Theoretical Limits of Detection in One 100-s Measurement
Wavelength-Dispersive Technique
with 50 ppm Hg Specimens

Mounting Method	A (100 mg)	B (500 mg)	C (100 mg)	D (100 mg)
Signal (counts)	3953	3092	3620	1031
Background (counts)	10746	13414	8082	8600
Standard Deviation (σ)[t]	103.6	115.8	89.9	92.7
S/N (Signal/σ)	38.2	26.7	40.3	11.1
Theoretical Limit of Detection	3.9 ppm	5.6 ppm	3.7 ppm	13.5 ppm

With the energy-dispersive apparatus, shown in figure 1, several different preparations were also tried. Method 1 was selected for these measurements. Specimens of 500 mg, 200 mg, 100 mg and 20 mg were tried (all doped with mercury at the 50 ppm level). The best signal-to-background ratio was achieved with the 100 mg specimen. The theoretical limit of detection with this specimen was 2.6 ppm mercury for a one-hour measurement.

After the energy-dispersive system was modified, specimens with a larger diameter could more easily be used. Coal specimens of 500 mg mounted by method 3 were found to give the highest signal-to-background ratio for mercury (fig. 4).

To obtain similar limits of detection from both energy-dispersive and wavelength-dispersive systems, sufficient counts must be accumulated by each system to give equivalent statistical results. Since the energy-dispersive system collects information on the whole x-ray spectrum, only a small portion of the signal is within the peak of interest while the wavelength-dispersive system collects information on only the peak of interest [2]. Therefore, with the energy-dispersive system, counts must be accumulated for a longer period of time than with the wavelength-dispersive system.

The theoretical limit of detection can be improved by counting for longer periods of time. For a 50 ppm mercury specimen, the theoretical limit of detection was 3.9 ppm for a 500 s counting time. When the time was doubled to 1000 s, the limit of detection dropped to 2.5 ppm; however, to further lower the limit of detection requires very long counting times (see fig. 5). The experimental limit of detection for the average of seven measurements for 500 s each was calculated to be 2.2 ppm at a 99% confidence interval.

There were no significant differences in the results obtained from either of the two experimental arrangements of the Y_2O_3 pellet. However, significantly lower backgrounds

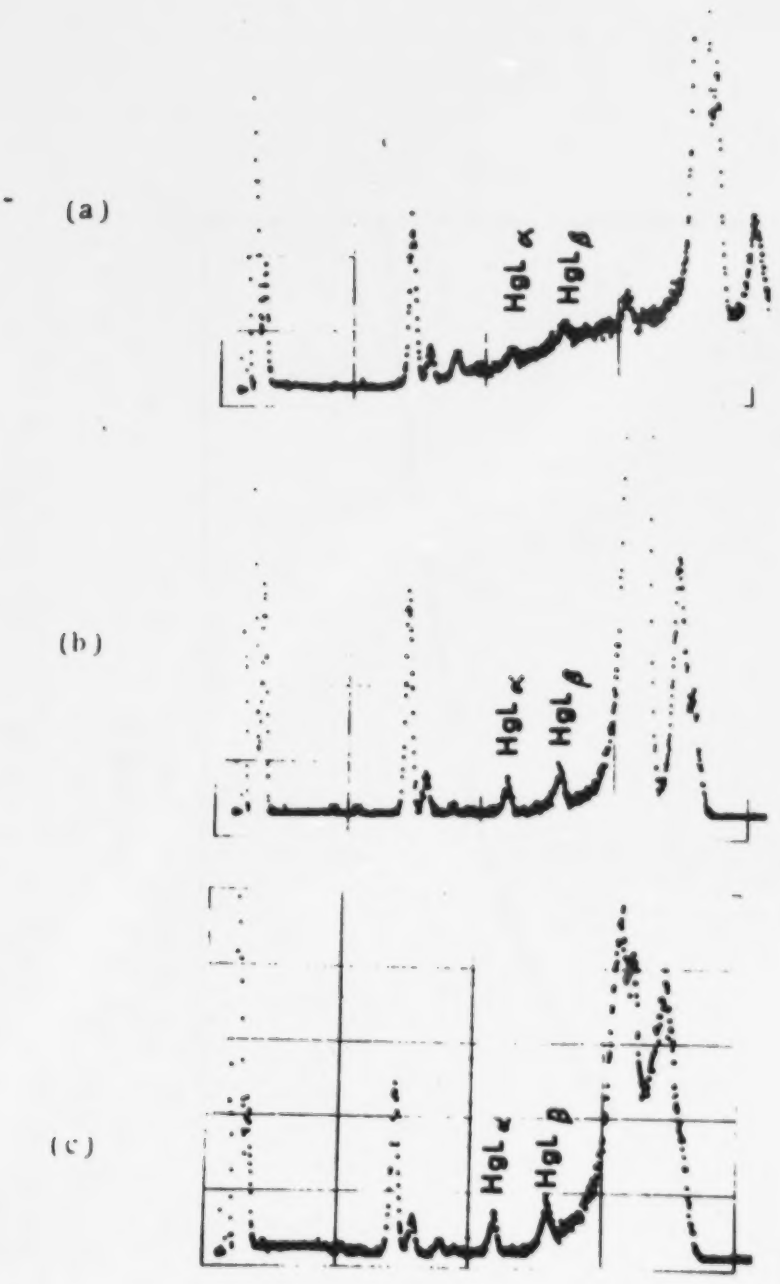

Figure 4. Energy-dispersive spectra of 0.125 weight percent mercury in coal. (a) direct excitation by Mo x ray tube; (b) excitation by Y_2O_3 secondary target; (c) excitation by Y_2O_3 filtered radiation.

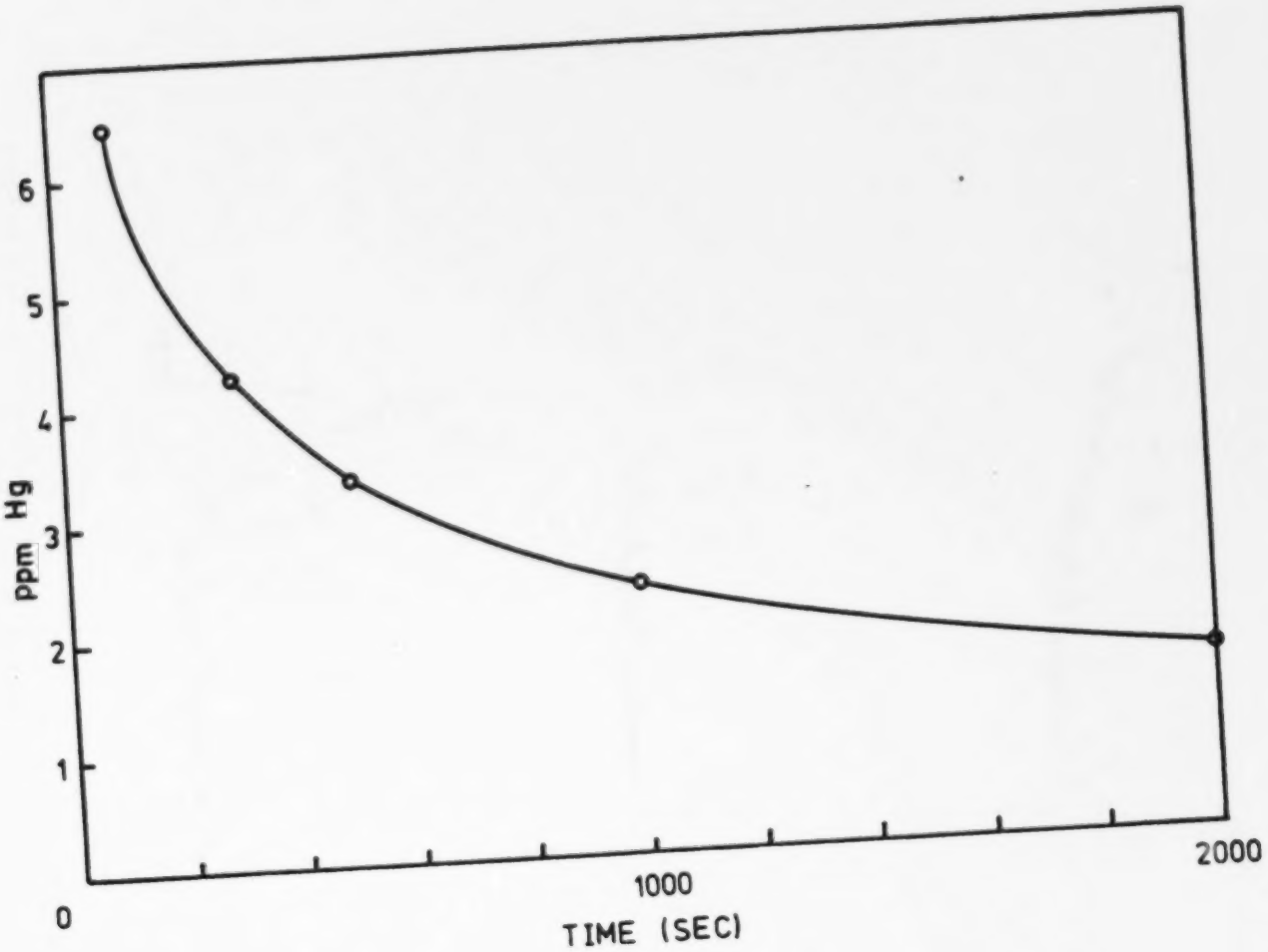

Figure 5. Limit of detecting as a function of time for Hg in coal. Energy-dispersive analysis on 50 ppm Hg specimen.

were obtained by carefully collimating the x-rays to reduce scattered x-rays in the specimen chamber. Collimators were placed between the secondary fluorescer and the specimen, and between the specimen and the detector (fig. 2b).

4. CONCLUSIONS

The lowest limit of detection determined by both the wavelength-dispersive and the energy-dispersive systems is approximately 2 ppm mercury in coal. For such results, the counting time with the energy-dispersive system must be increased by a factor of ten over that with the wavelength-dispersive system. However, with the energy-dispersive system, the concentrations of other elements may be simultaneously determined along with mercury. With a wavelength-dispersive system, the number of elements simultaneously determined is limited to the number of crystal spectrometers on the system.

At the present time, neither of these x-ray fluorescence techniques is sensitive enough to determine mercury in natural coal; however, these techniques may be satisfactory for other materials. Besides coal, the limit of detection for mercury will be determined in fly ash, Fe_2O_3, PbO and CuO. Several other elements (such as lead, arsenic, cadmium and vanadium) are also important in these materials, and will be determined. Along with these measurements, we will continue to examine further techniques for improving our limits of detection.

5. REFERENCES

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